UNIVERSITY OF PENNSYLVANIA

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A DISSERTATION

IN CHEMISTRY

PRESENTED TO THE FACULTY OF THE GRADUATE SCHOOL IN
PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY

JAY HAROLD QUINN

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THE TITRATION OF SILVER WITH POTASSIUM IODIDE.

USE OF FOUR SELECTED OXIDIZING AGENTS AND STARCH AS INDICATORS.

BY

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A method of determining silver by titration with standard potassium iodide in the presence of starch and ceric ions has been described (1, 2, 4, 8, 9). The advantages of this method over the Gay-Lussac and Volhard methods led the authors to investigate its further application; namely, the titration of silver with a standard potassium iodide solution in the presence of four other selected oxidizing agents and starch as indicators. Of the oxidizing agents selected from a table of oxidation-reduction potentials, it was found that potassium dichromate, potassium permanganate, potassium bromate, or potassium iodate gave satisfactory results. This method is believed to be applicable to any properly prepared solution of silver free from interfering substances, such as mercury, palladium, or thallous salts.

Titrations were carried out varying the amounts of reagents so as to establish the best conditions for the greatest degree of accuracy. Results were obtained by titrating in the presence of elements sometimes associated with silver to test for possible interference.

REAGENTS.

All chemicals were C.P. analytical grade. Silver nitrate and potassium iodide were twice recrystallized and powdered. The silver nitrate was dried at 120° C. for one hour and the potassium iodide was dried at 180° C. for one hour. Standard 0.1 N solutions of silver nitrate and potassium iodide were prepared by weight.

Potassium dichromate, potassium permanganate, potassium bromate, and potassium iodate were recrystallized and dried in a desiccator over calcium chloride. Solutions 0.1 N as oxidizing agents were prepared from these salts.

Salts of arsenic, bismuth, cobalt, copper, iron, lead, manganese, mercury, nickel, and zinc were used without purification.

The starch solution was prepared by dissolving 0.5 gram of soluble starch in 5 ml. of cold water. This solution was poured into 95 ml. of boiling water and boiled for a few minutes. The 0.5 per cent. starch solution was kept in a glass stoppered bottle.

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PROCEDURE.

Weigh a sample containing between 1 to 2 grams of silver into a 400 ml. beaker and add 10 ml. of nitric acid (1:1). Heat the beaker until the sample is dissolved and add 20 ml. of distilled water. Continue the heating until the oxides of nitrogen are removed as shown by the disappearance of the brown color. Transfer this solution to a 250 ml. volumetric flask and dilute to the mark with distilled water.

Pipet a 25 ml. aliquot of the dilution into a 250 ml. Erlenmeyer flask containing 35 ml. of approximately 6 N sulfuric acid. Dilute the solution to approximately 100 ml. with distilled water.

After the addition of 1 drop of 0.1 N potassium permanganate, or 3 drops of 0.1 N potassium dichromate, potassium bromate, or potassium iodate, add 3 ml. of freshly prepared 0.5 per cent. starch solution. Titrate with the standard 0.1 N potassium iodide solution to the first permanent blue-green color. Run a blank determination under identical conditions but omit the sample.

EXPERIMENTAL.

The conditions necessary for the highest accuracy were first determined. Sufficient pure, dry potassium iodide to give a 0.1 N solution was weighed, transferred to a liter volumetric flask, and diluted to the mark. Solutions of known strength of pure silver nitrate were similarly prepared. Accurately measured volumes of the silver nitrate solution were transferred to 250 ml. Erlenmeyer flasks. Increasing amounts of sulfuric acid were added and the solutions diluted to 100 ml. with distilled water. The amounts of oxidizing agent and starch recommended in the procedure were added and the solutions titrated.

In a similar manner the amounts of the oxidizing agents and the starch were varied until the optimum conditions were determined.

Using the best conditions determined as above, increasing amounts of different elements were added to the solution to be titrated. In this manner, the tests for possible interference were made.

Three alloys were analyzed for silver by the Gay-Lussac method, the Volhard method, and the method presented here. The procedure used for the Gay-Lussac method is given by Kolthoff and Furman (6). The procedure used for the Volhard method is that given by Hillebrand and Lundell (5). Potassium permanganate was used as the oxidizing agent in the potassium iodide method with alloy number one that contained silver, copper, and zinc. Potassium dichromate was used as the oxidizing agent with alloy number two that contained silver and copper. Potassium bromate was the oxidizing agent used with alloy number three that contained silver, copper, and zinc.

An additional comparison of the accuracy of the method was obtained by using ceric ammonium sulfate as the oxidizing agent in the procedure described by Bloom and McNabb (1).

DISCUSSION.

One of the advantages of the method presented here is the choice of one of four oxidizing agents and starch as indicators in the titration of silver with a standard potassium iodide solution. Another advantage is the use of a standard potassium iodide solution prepared by weight, making a standardization unnecessary. The chief advantage is the sharp and easily detected end-point which eliminates one source of uncertainty found in the Gay-Lussac and Volhard methods.

Mulder (5) reported that many elements interfered in the Gay-Lussac method. Mercury was the most harmful. Bismuth readily hydrolyzed to render the end-point indistinct.

When Dewey (3) studied the effect of various elements on the Volhard method he found several that interfered. Mercury salts interfered because they formed slightly dissociated mercury thiocyanate. Copper salts formed dark colored copper thiocyanate that obscured the end-point. Large quantities of nickel and cobalt interfered because their color made the end-point difficult to detect.

When using the potassium iodide method presented here no appreciable difference was obtained when 100 to 200 milligrams of silver were titrated in the presence of separate solutions of arsenic, bismuth, cobalt, copper, iron, lead, manganese, nickel, and zinc. These various elements were present in concentrations ranging from 4 to 300 milligrams.

Copper salts might have been expected to interfere in this procedure due to reaction with potassium iodide to form cuprous iodide and iodine. Iron might also have been expected to interfere because ferric ions oxidize potassium iodide in acid solutions. The oxidation-reduction potentials of any of the oxidizing agents, however, are much stronger than those of cupric or ferric ions. A small amount of potassium iodide, therefore, would be oxidized by the added oxidizing agent before reaction with cupric or ferric ions could occur, and there would be no interference.

Lead often found with silver does not interfere because of the insolubility of lead sulfate.

Increasing the amounts of sulfuric acid, oxidizing agents, or starch indicated that with very large amounts of these reagents high results were obtained. When using amounts recommended in the procedure, satisfactory values resulted.

Attempts to substitute nitric acid or acetic acid for the sulfuric acid were not successful.

Analytical results given in Tables I to IV show the accuracy of the method. These may be compared with results obtained using the ceric ammonium sulfate procedure which are shown in Table V.

In Table VI results are given for the analyses of three alloys in which the Gay-Lussac and Volhard procedures were selected for comparison.

TABLE I.

Potassium Dichromate and Starch as Indicators.

Ag Taken, Gram	Ag Found, Gram	Difference, Gram
0.0539	0.0541	+0.0002
0.0539	0.0540	+0.0001
0.0539	0.0541	+0.0002
Ag Taken, Gram	**Ag Found, Gram**	**Difference, Gram**
0.1079	0.1081	+0.0002
0.1079	0.1082	+0.0003
0.1079	0.1081	+0.0002
Ag Taken, Gram	**Ag Found, Gram**	**Difference, Gram**
0.2158	0.2162	+0.0004
0.2158	0.2163	+0.0005
0.2158	0.2161	+0.0003

TABLE II.

Potassium Permanganate and Starch as Indicators.

Ag Taken, Gram	Ag Found, Gram	Difference, Gram
0.0539	0.0540	+0.0001
0.0539	0.0539	0.0000
0.0539	0.0540	+0.0001
Ag Taken, Gram	**Ag Found, Gram**	**Difference, Gram**
0.1079	0.1082	+0.0003
0.1079	0.1082	+0.0003
0.1079	0.1081	+0.0002
Ag Taken, Gram	**Ag Found, Gram**	**Difference, Gram**
0.2158	0.2161	+0.0003
0.2158	0.2162	+0.0004
0.2158	0.2163	+0.0005

TABLE III.

Potassium Bromate and Starch as Indicators.

Ag Taken, Gram	Ag Found, Gram	Difference, Gram
0.0539	0.0541	+0.0002
0.0539	0.0541	+0.0002
0.0539	0.0540	+0.0001
Ag Taken, Gram	**Ag Found, Gram**	**Difference, Gram**
0.1079	0.1081	+0.0002
0.1079	0.1082	+0.0003
0.1079	0.1081	+0.0002
Ag Taken, Gram	**Ag Found, Gram**	**Difference, Gram**
0.2158	0.2162	+0.0004
0.2158	0.2162	+0.0004
0.2158	0.2163	+0.0005

TABLE IV.

Potassium Iodate and Starch as Indicators.

Ag Taken, Gram	Ag Found, Gram	Difference, Gram
0.0539	0.0540	+0.0001
0.0539	0.0541	+0.0002
0.0539	0.0542	+0.0003
Ag Taken, Gram	Ag Found, Gram	Difference, Gram
0.1079	0.1082	+0.0003
0.1079	0.1081	+0.0002
0.1079	0.1081	+0.0002
Ag Taken, Gram	Ag Found, Gram	Difference, Gram
0.2158	0.2162	+0.0004
0.2158	0.2163	+0.0005
0.2158	0.2162	+0.0004

TABLE V.

Ceric Ammonium Sulfate and Starch as Indicators.

Ag Taken, Gram	Ag Found, Gram	Difference, Gram
0.0539	0.0540	+0.0001
0.0539	0.0541	+0.0002
0.0539	0.0540	+0.0001
Ag Taken, Gram	Ag Found, Gram	Difference, Gram
0.1079	0.1081	+0.0002
0.1079	0.1082	+0.0003
0.1079	0.1081	+0.0002
Ag Taken, Gram	Ag Found, Gram	Difference, Gram
0.2158	0.2162	+0.0004
0.2158	0.2163	+0.0005
0.2158	0.2161	+0.0003

TABLE VI.

Comparison of Methods.

Alloy—(1)	Method Used	Per Cent. Silver
(Ag, Cu, Zn)	Gay-Lussac	50.23
		50.21
	Volhard	50.31
		50.31
	Potassium Iodide	50.34
		50.34
Alloy—(2)		
(Ag, Cu)	Gay-Lussac	89.75
		89.72
	Volhard	89.81
		89.90
	Potassium Iodide	89.89
		89.90

TABLE VI.—*Continued.*

Alloy—(3)	Method Used	Per Cent. Silver
(Ag, Cu, Zn)	Gay-Lussac	30.82
		30.82
	Volhard	30.85
		30.85
	Potassium Iodide	30.89
		30.89

SUMMARY.

A method was investigated for the volumetric determination of silver by titration with potassium iodide in the presence of starch and four selected oxidizing agents as indicators. The results obtained by this method show satisfactory levels of precision and accuracy, and are substantially identical with results by the Gay-Lussac and Volhard methods.

The presence of the following metals does not interfere in the method: arsenic, bismuth, cobalt, copper, iron, lead, manganese, nickel, and zinc. Metals such as mercury and palladium that form insoluble iodides must be removed before titrating the silver.

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